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Neutron diffraction study of tin-substituted Mg-Zn ferrites

A K Ghatage, S A Patil and S K Paranjpe*

Department of Physics, Shivaji University, Kolhapur-416 004, Maharashtra, India

*Solid State Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400 085, India

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Abstract : The magnetic behaviour of tin-substituted Mg-Zn ferrites has been studied by powder neutron diffraction and magnetic measurements. The net magnetic moment (n_B) and Curie temperature T_c decreases with increase in tin content. The experimental values of n_B obtained from neutron diffraction and magnetic measurements are found to be less than those calculated with Neel's model. Gilleo's model has also been used to calculate n_B and T_c values. These values are higher than the experimental ones. It is concluded that canted spin arrangement is favoured in these ferrites.

Keywords : Ferrites, magnetic structure, neutron diffraction

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1. Introduction

A wide variety of ferrite materials has been developed for application in electronic and microwave industries. The cubic spinel structure permits to substitute cations selectively on the octahedral and/or tetrahedral sites. This helps in modifying electrical and magnetic ordering in these systems. Extensive work has been done by various workers to upgrade the properties of ferrites by substituting different types and amounts of impurities. It has been reported that by addition of small amount of tetravalent ions like titanium or tin, electrical and magnetic properties of basic Ni-Zn and Mg-Zn ferrites are significantly influenced [1–3]. An anomaly in magnetisation was observed in tin substituted Mg ferrite [4]. It was also stated that for lower contents of tin, it occupies only B-site and as tin-content increases, it occupies both A and B sites [3]. In order to understand the cation distribution and its effect on the magnetisation behaviour, we have carried out neutron

diffraction, low field ac susceptibility and magnetisation measurements on tin substituted Mg-Zn ferrites.

2. Experimental

The samples of the series $Mg_{0.7+x}Zn_{0.3}Sn_xFe_{2-2x}O_4$ (with $x = 0.0, 0.1, 0.3$) were prepared by ceramic method. AR grade MgO, ZnO, SnO_2, Fe_2O_3 were weighed in required proportions and mixed thoroughly. These powders were pre-sintered in air at 800°C for 10 hours, then milled and pellets were made and finally sintered at 1100°C for 24 hours in air and then slowly cooled. The formation of single phase was confirmed by X-ray diffraction using CuK_α radiation. Magnetisation measurements were carried out on high field loop tracer. AC-susceptibility (χ_{ac}) was measured using low field ac-susceptibility technique, and Curie temperature was obtained from the normalised susceptibility *versus* temperature plots.

Neutron diffraction measurements were carried out on polycrystalline samples using the position sensitive detector based powder diffractometer at Dhruva reactor at BARC. Monochromatic neutrons having wavelength of 1.094 Å were used for the experiment. The samples were packed in cylindrical vanadium containers. Diffraction profiles were recorded at 300 K in the angular range (2θ) 10° to 100°. The patterns showed single phase compounds except for a small unidentified impurity phase for $x = 0.3$ sample. The X-ray patterns, however, did not give any indication of such an impurity phase. The data were analysed using Rietveld profile refinement technique for both chemical and magnetic structures [5,6].

3. Results and discussion

As the compounds are magnetically ordered at 300 K, only higher angle data, where the magnetic contribution to the Bragg peaks is negligible, were first refined to get the chemical structure [7]. For the system under study, the occupancies of some of cations were fixed by considering their site preference. It is well known that Zn has strong preference for A-site. In the refinement, therefore, all the Zn ions were put on the A-site. The oxygen position parameter (u), the isotropic temperature factor (B) and lattice constant (a) were varied in addition to the profile half width parameters. The site occupancies of Fe, Sn and Mg were varied independently within the constraint of satisfying the stoichiometry of the system. The fitted and observed profiles for the composition $x = 0.0$ are shown in Figure 1, along with the difference plot.

The results of the refinement are summarised in Table 1. It is observed that the lattice parameter a increases with increase in Mg and Sn content, which may be a direct consequence of the larger ionic radii of the Mg and Sn (*i.e.* 0.78 Å and 0.69 Å, respectively) as compared to Fe (0.67 Å). The oxygen position parameter was found to be almost constant ($u = 0.258$) for all the samples. From u-parameter it is concluded that the

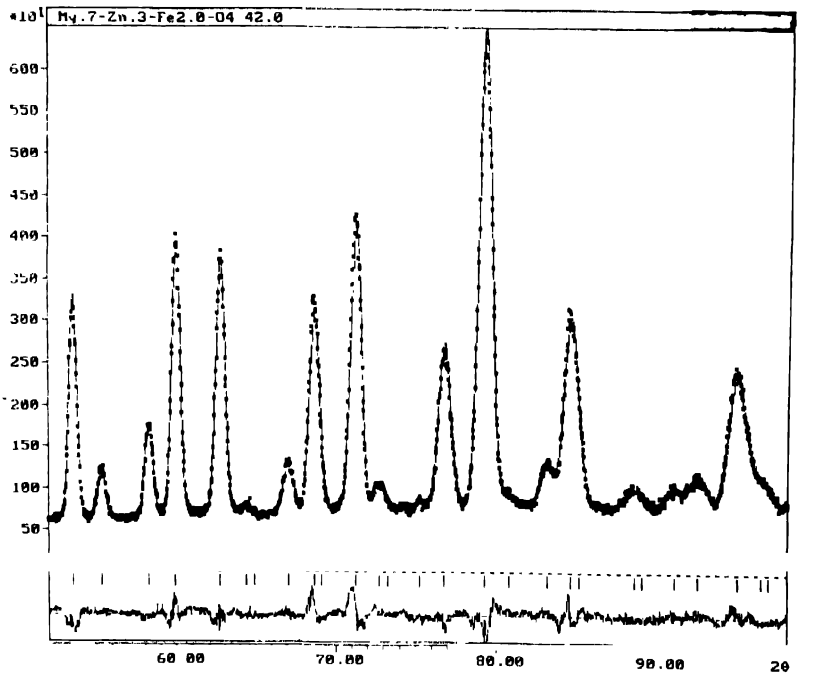

Figure 1. Pattern of nuclear profile refinement for, $x = 0.0$

Table 1. Parameters obtained from Rietveld profile refinement, for $Mg_{0.7+x}Zn_{0.3}Sn_xFe_{2-2x}O_4$ system

x Parameter	0	0.1	0.3
Lattice constant a (Å)	8.385 (8)	8.423 (8)	8.460 (6)
Oxygen parameter u (Å)	0.2579	0.258	0.2582
Temperature factor B (cm^2)	0.50	0.43	0.33
Cation distribution	$(Zn_{0.3}Mg_{0.056}Fe_{0.644})$ $[Mg_{0.644}Fe_{1.356}]$	$(Zn_{0.3}Mg_{0.138}Fe_{0.562})$ $[Mg_{0.662}Sn_{0.1}Fe_{1.238}]$	$(Zn_{0.3}Mg_{0.266}Fe_{0.424})$ $[Mg_{0.734}Sn_{0.3}Fe_{0.966})$
b_A	0.8148	0.7807	0.7178
b_B	0.8198	0.7995	0.7515
R_p	3.75	3.85	4.76
R_{wp}	4.7	4.84	6.04
R_{exp}	2.74	3.6	2.81
R_B	3.42	4.62	5.93
	From magnetic structure analysis		
μ_A	2.1 (1)	1.85 (6)	1.22 (4)
Free ion	2.35	1.99	1.44
μ_B	1.99 (6)	1.65 (6)	0.83 (6)
Free ion	2.49	2.19	1.65

coordination of Fe ion is very little affected by changes in the compositional parameter. From the cation distribution it is observed that Sn occupies B-site. Mg ion, however, occupies both the sites.

The A-site magnetic moment was deduced from the intensities of (220) and (422) reflections. The structure factors of both these reflections have contribution from A-site magnetic moment only. The B-site moment was obtained using (222) reflection, the intensity of which depends only on B-site magnetic moment. These values were used as initial parameters for magnetic profile refinement. The values obtained after refinement are almost same as those derived from the intensities. The fitted profile with magnetic reflections for one of the compositions $x = 0.0$ is shown in Figure 2. The values of the magnetic moments obtained are given in Table 2. The magnetic moments determined from

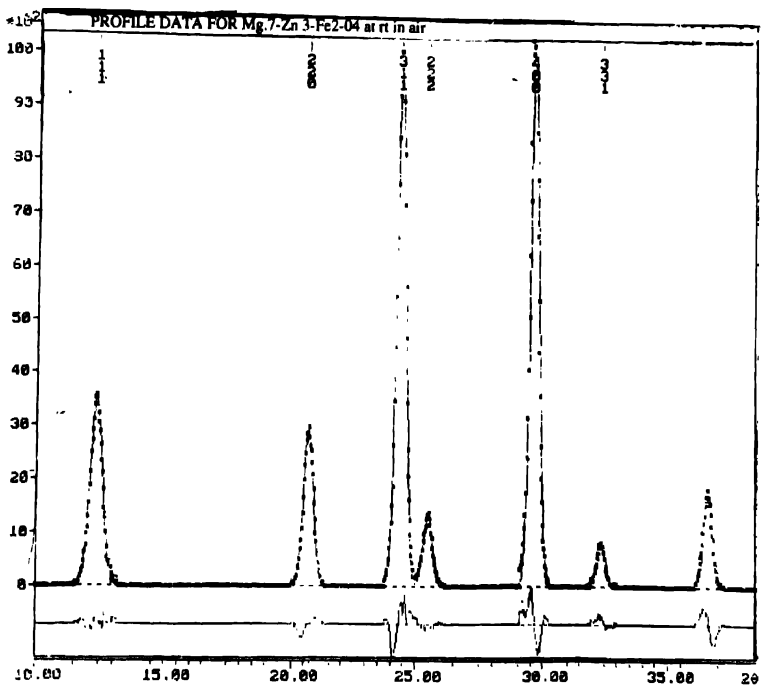

Figure 2. Pattern of (nuclear + magnetic) refinement for, $x = 0.0$.

hysteresis and from neutron study for different values of x are also given in Table 2. These values are in good agreement with each other and decrease with increase in x.

The magnetisation behaviour in ferrites is explained on the basis of Neel's molecular field model. Considering the magnetic ions on both tetrahedral (A) and octahedral (B) sites, the possible exchange interactions are the two intrasite (AA and BB) and one intersite (AB). Amongst the three magnetic interactions, the intersite AB interaction is the strongest. In this

model collinear arrangement of magnetic moments of individual site is presumed *i.e.* the magnetic ions on each sublattice are ferromagnetically aligned with an opposite alignment of intersite moments. The net magnetisation is the vector sum of octahedral (B) and tetrahedral (A) site magnetisations. The n_B values are calculated using Neel's two sublattice model with suitable correction for the Brillouin function and using the cation distribution

Table 2. Magnetic moment and Curie temperature from various methods for $Mg_{0.7+x}Zn_{0.3}Sn_xFe_{2-2x}O_4$ system.

content	Magnetic moment (n_B)				Curie temperature (K)	
x	From neutron	From magnetic measurement	From Neel's model	From Gilleo's model	From susceptibility	From Gilleo's model
0	1.88	1.71	3.58	3 4	590	600
0 1	1.45	1.54	3.38	3	520	577
0.3	0 45	0 54	2 66	1 78	450	522

obtained from neutron data. These values are given in Table 2. The n_B values show a decreasing trend with x. The experimental n_B values are lower than the theoretical ones indicating a deviation from the collinear arrangement of moments.

4. Gilleo's model

The magnetic moment and Curie temperature were calculated using the Gilleo's model [8,9]. With the assumption that magnetic moment actively participates in ferrimagnetism only when it interacts with two or more magnetic ions in different coordination. Gilleo has proposed a statistical model which neglects intrasublattice interaction and thus no canted spin is considered.

If K is the fraction of Fe^{3+} ions which are replaced by nonmagnetic ions at one site; for each $(1-K)$, the probability of one ion being linked with other m ions is

$$P_n(m) = (n_m)K^{n-m}(1-K)^m.$$

The probability E that an ion is linked with no or atmost one magnetic ion is

$$E = P_n(m) = nK^{n-1} - (n-1)K^n.$$

In the present system

$$M_m Fe_{3-m} O_4,$$

where m is the amount of the nonmagnetic cation M. The cation distribution is given as

$$\left(M_{xm}Fe_{1-xm}\right)\left[M_{(1-x)m}Fe_{2-(1-x)m}\right].$$

The magnetic moment is given by

$$M_B = M^{(0)} - M^{(1)},$$

where $M^{(0)} = 2 \times 5(1-K_0)[1-E_0(K_t)]$

and $M^{(1)} = 1 \times 5(1-K_t)[1-E_t(K_0)]$.

Here, $K_t = xm$ (at A site) and $K_0 = (1-x)\,m/2$ (at B site),

$n_{AB} = 12$ and $n_{BB} = 6$,

and $E_0(K_t) = 6K - 5K, E_t(K_0) = 12K^{11} - 11K^{12}$.

Thus, calculated magnetic moment values are given in Table 2 and are higher than the observed values.

The theoretical calculations to estimate the Curie temperature for spinel ferrites are given by Gilleo [8]. According to the model the Curie temperature is proportional to the number of active linkages per magnetic ion per formula unit and is cast in the form :

$$T_c = 3x(1-x)[1-E_0(K_t)][1-E_t(K_0)](3-m)T_0/2[x(1-E_0(K_t) + (1-x)(1-E_t(K_0)],$$

where T_0 is a constant. Milligan *et al* [10] have evaluated T_0 for $MgFe_2O_4$ with cation distribution $Mg_{0.1}Fe_{0.9}[Mg_{0.9}Fe_{1.1}]$, and Curie temperature 440°C. The T_0 was calculated to be 961°C. The calculated Curie temperatures (T_c) are given in Table 2. The theoretically calculated T_c values are higher than those obtained from experiment, the difference being large for ferrites with higher Sn-concentration.

5. Non-collinear structure

From Table 1, it is observed that the A-site moment is close to the free ion value. The B-site moments on the other hand, are smaller than their estimated free ion values, suggesting that the B-site moments are noncollinear. The occurrence of localised canting has been reported in tetravalent and zinc mixed ferrites [11]. A canting of Yaffet-Kittel [12] type on the B-site and spatial ordering of the transverse spin components of the magnetic moment should give rise to the (200) reflection [6], which is purely magnetic in nature. None of the systems studied here show this reflection. However, the absence of (200) does not rule out the possibility of a canted structure as has been shown in many cubic spinels like $ZnCr_{2x}Ga_{2-2x}O_4$ [13] and $Zn_xCo_{1-x}FeCrO_4$ [13]. Such a behaviour can be explained on the basis of a long range ferrimagnetic ordering of the longitudinal component with the A-site moments, and a disordered normal component. The system under study could have similar behaviour.

6. ac-susceptibility

The temperature dependence of the normalised ac susceptibility for the series of samples is shown in Figure 3. From the nature of these plots, it is observed that χ_{ac} remains almost constant in all the samples until the temperature reaches nearer to Curie temperature.

The normalised ac susceptibility χ_{ac} drops rapidly to zero at Curie temperature. However, tailing effect is observed for higher content of Sn.

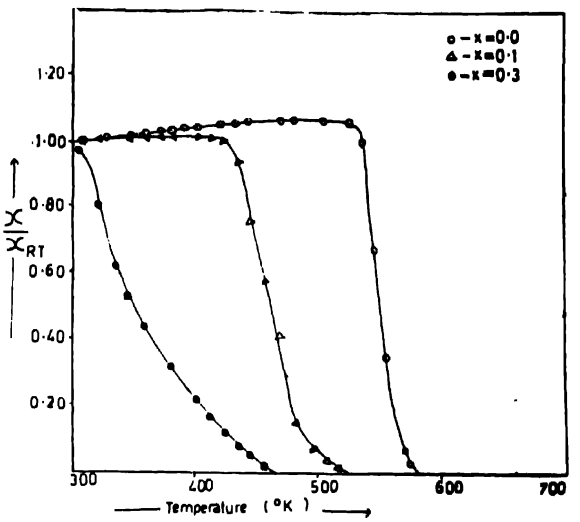

Figure 3. Variation of susceptibility with temperature for $Mg_{0.7+x}Zn_{0.3}Sn_xFe_{2-2x}O_4$ system.

A polycrystalline magnetic material consists of three types of domain states, *viz.* multidomain (MD), singledomain (SD) and superparamagnet (SP). It has been observed that for MD samples χ_{ac} does not change appreciably with temperature and drops off sharply at Curie temperature. For SP samples χ_{ac} decreases with temperature and become zero at Curie temperature. For SD samples χ_{ac} increases and shows a maxima at blocking temperature T_b and then decreases to zero at Curie temperature. Murthy and Nandikar [13] have explained the magnetic behaviour of ferrites on the basis of shapes of χ_{ac} curves. From these observations and based on the concept given above it can be concluded that the samples under study contain MD states. It is also noted that tailing in χ_{ac} curve near Curie temperature is due to canting in ferrites. Our samples show tailing effect for higher content of Sn. This observation supports our conclusion of the presence of a canted magnetic ordering in these materials.

7. Conclusion

The neutron diffraction and magnetic measurements on the series of Sn substiiuted Mg-Zn ferrites show that the magnetic moment on the octahedral site is reduced and can be explained on the basis of a canted spin arrangement.

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References

[1] Usha Varashney and R K Puri *IEEE. Trans Magn.* **25** 3109 (1989)

[2] A R Das, V S Ananthan and D C Khan *J Appl. Phys.* **57** 4189 (1985)

[3] S S Suryavanshi, S R Savant and S A Patil *Indian J Pure Appl Phys.* **31** 500 (1993)

[4] D R Sagar, Prakash Chandra, S N Chattarjee and P Kishan *Proc ICF-5 India, Advances in Ferrites* ed C M Srivastava and M J Patni (New Delhi . IBH and Oxford) (1989)

[5] H M Rietveld *Acta Cryst* **22** 151 (1967)

[6] H M Rietveld *J Appl Cryst* **2** 65 (1969)

[7] R A Young and D B Wiles *J. Appl Cryst.* **10** 262 (1982)

[8] M A Gilleo *J Phys Chem. Solids* **13** 33 (1960)

[9] Chen Yang and He Rui-Yun *J Mag. Materials* **116** 231 (1992)

[10] W Milligan, Y Tamai and J T Richardson *J Appl Phys.* **34** 2093 (1963)

[11] R C Srivastava, D C Khan and A R Das *Phys. Rev* **B41** 12514 (1990)

[12] N S Satya Murthy, M G Natera, S I Youssetf, R J Begum and C M Srivastava *Phys Rev* **181** 969 (1969)

[13] C R K Murthy and N G Nandikar *Pramana* **13** 473 (1979)